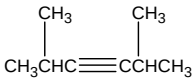
Chapter 8

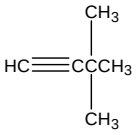
8.1 Name the following compounds:

(a)



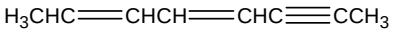
2,5-dimethyl-3-hexyne

(b)



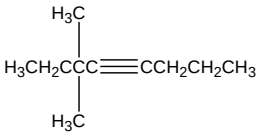
3,3-dimethyl-1-butyne

(c)



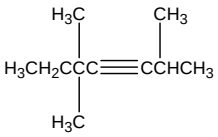
2,4-octadiene-6-yne

(d)



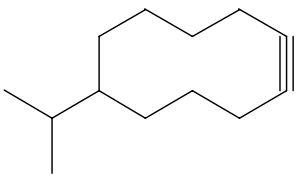
3,3-dimethyl-4-octyne

(e)



2,5,5-trimethyl-3-heptyne

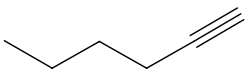
(f)



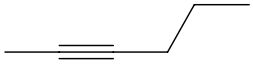
6-isopropyl-cyclodecyne

8.2 There are seven isomeric alkynes with the formula C_6H_{10}. Draw and name them.

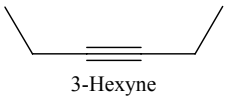
Solution:



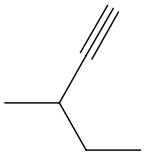
1-Hexyne



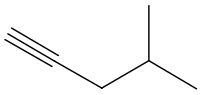
2-Hexyne



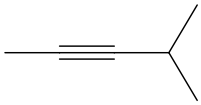
3-Hexyne



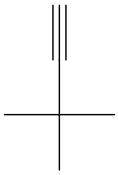
3-methyl-1-pentyne



4-methyl-1-pentyne



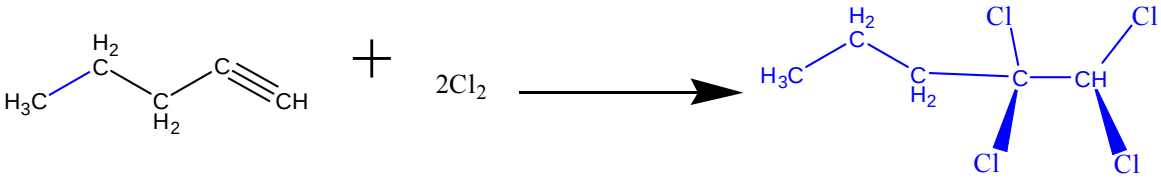
4-methyl-2-pentyne



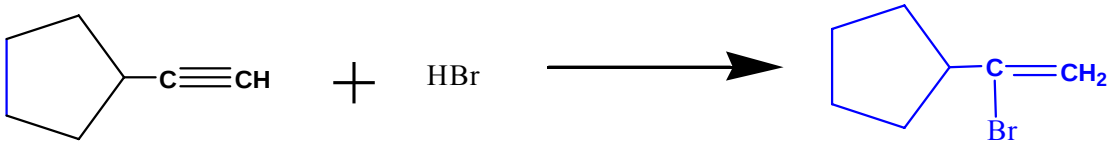
3,3-dimethyl-1-butyne

8.3 What products would you expect from the following reactions?

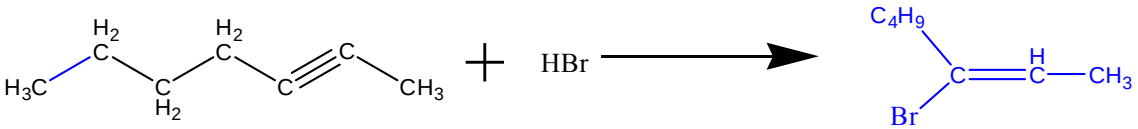
(a)



(b)

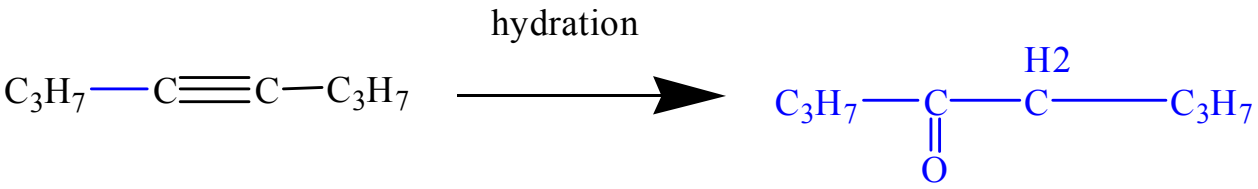


(c)

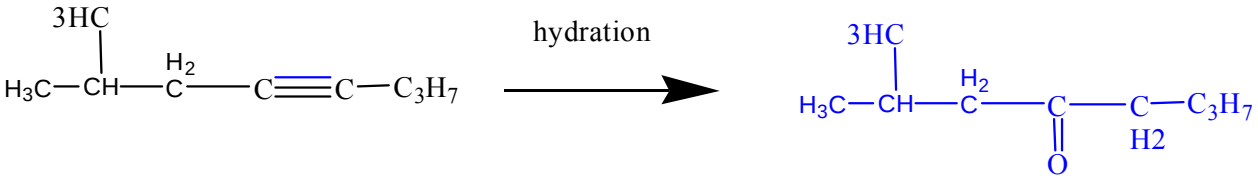


8.4 What product would you obtain by hydration of the following alkynes?

(a)



(b)



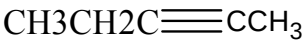
8.5 What alkynes would you start with to prepare the following ketones?

(a) 

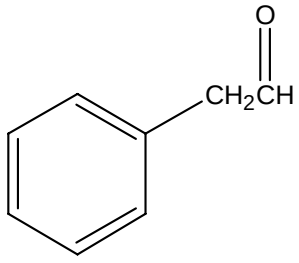
(b) 

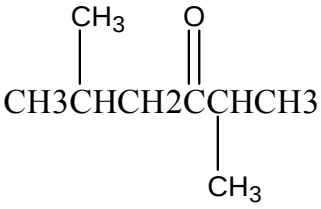
Solution:

(a) 

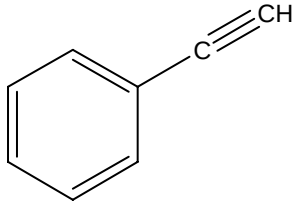
(b) 

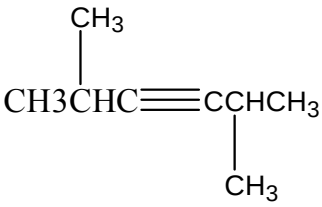
8.6 What alkyne would you start to prepare each of the following compounds by a hydroboration / oxidation reaction?

(a) 

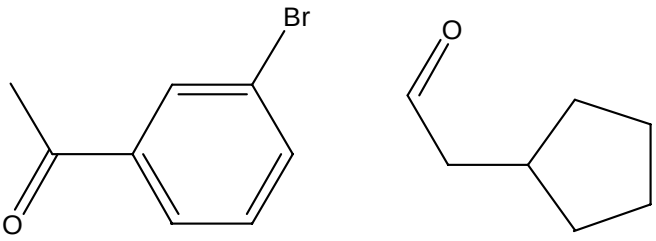
(b) 

Solution:

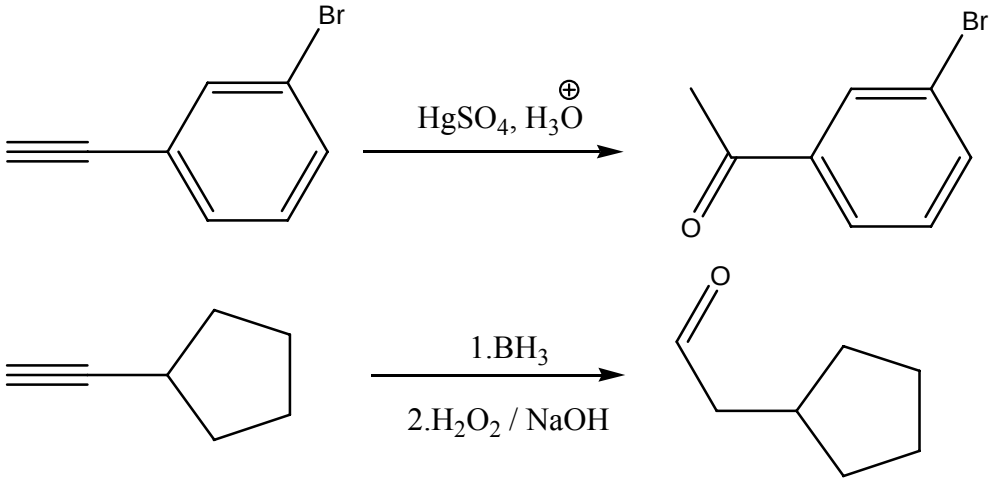
(a) 

(b) 

8.7 How would you prepare the following carbonyl compounds starting from an alkyne?



solution:



8.8 Using any alkyne needed, how would you prepare the following alkenes?

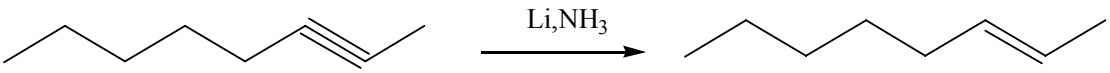
(a) trans-2-Octene

(b) cis-3-Heptene

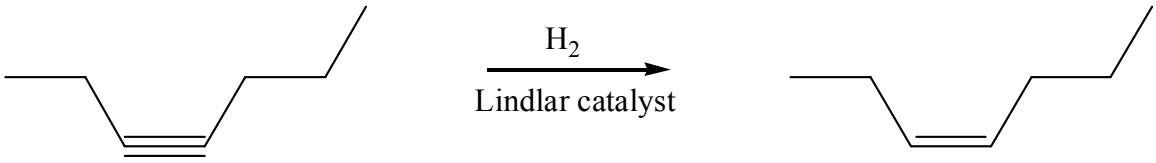
(c) 3-Methyl-1-pentene

solution:

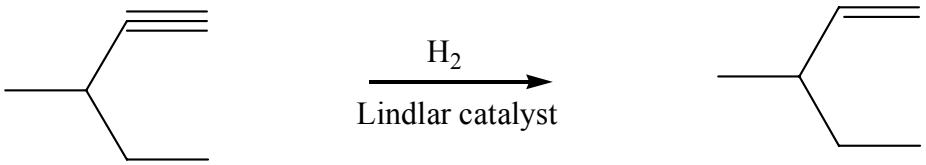
(a)



(b)

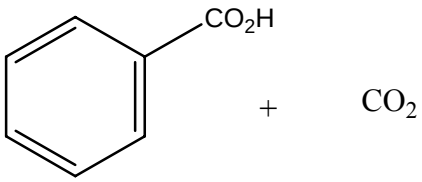


(c)



8.9 Propose structures for alkynes that give the following products on oxidative cleavage by $KMnO_4$:

(a)

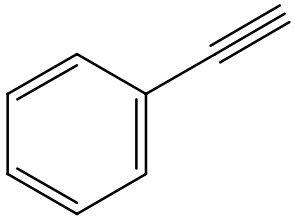


(b)

$2CH_3(CH_2)_7CO_2H + HO_2C(CH_2)_7CO_2H$

Solution: The structure is:

(a)



(b)

$CH_3(CH_2)_7C{\equiv}C(CH_2)_7C{\equiv}C(CH_2)_7CH_3$

8.10

The pK_a of acetone, CH_3COCH_3, is 19.3. Which of the following bases is strong enough to deprotonate acetone?

(a) KOH (pK_a of H_2O = 15.7) (b) $Na^+ {}^-C{\equiv}CH$ (pK_a of C_2H_2 = 25)

(c) $NaHCO_3$ (pK_a of H_2CO_3 = 6.4) (d) NaOCH3 (pK_a of CH_3OH = 15.6)

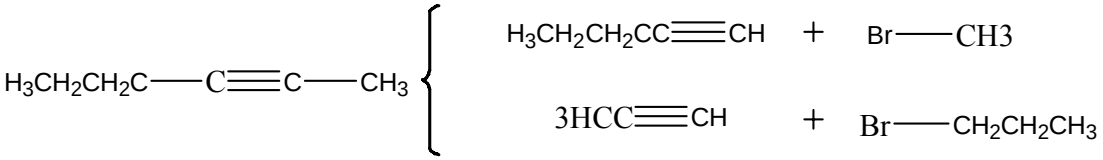
Solution: (b)

Because $pK_a(C_2H_2) > pK_a(CH_3COCH_3)$

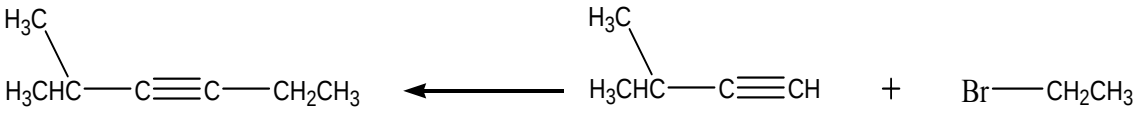
8.11 Show the terminal alkyne and alkyl halide from which the following products can be obtained. If two routes look feasible, list both.

Answer:

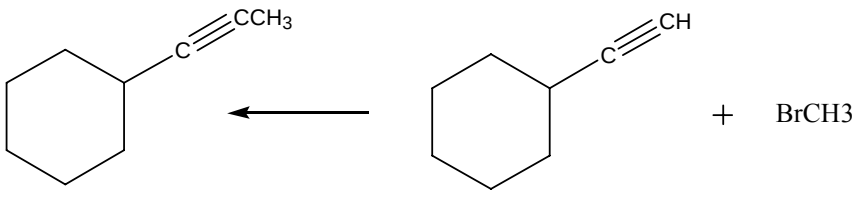
(a)



(b)



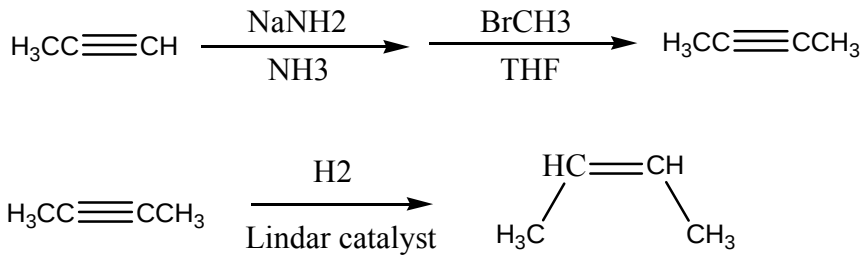
(c)



8.12 How would you prepare cis-2-butene starting from propyne, an alkyl halide, and any other reagents needed? This problem can't be worked in a single step. You'll have to carry out more than one

reaction.

Answer:

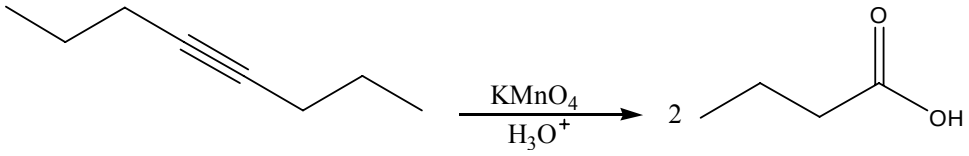


8.13 Beginning with 4-octyne as your only source of carbon and using any inorganic reagents necessary, how would you synthesize the following compounds?

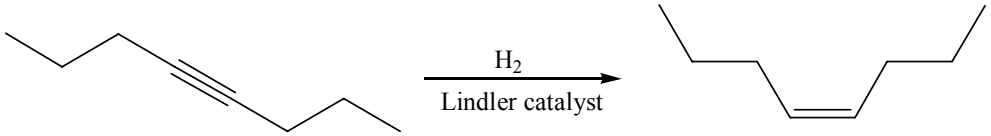
(a) Butanoic acid (b) cis-4-Octene (c) 4-Bromooctane

(d) 4-Octanol (4-hydroxyoctane) (e) 4,5-Dichlorooctane

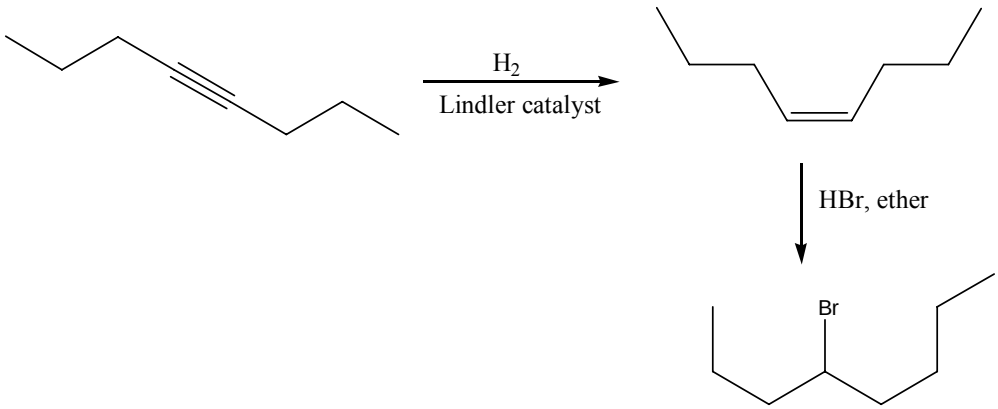
Solution: (a)



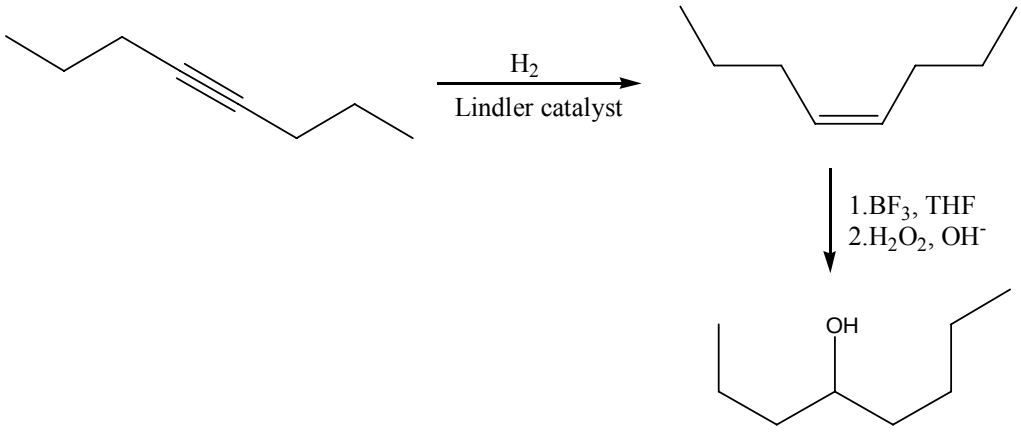
(b)



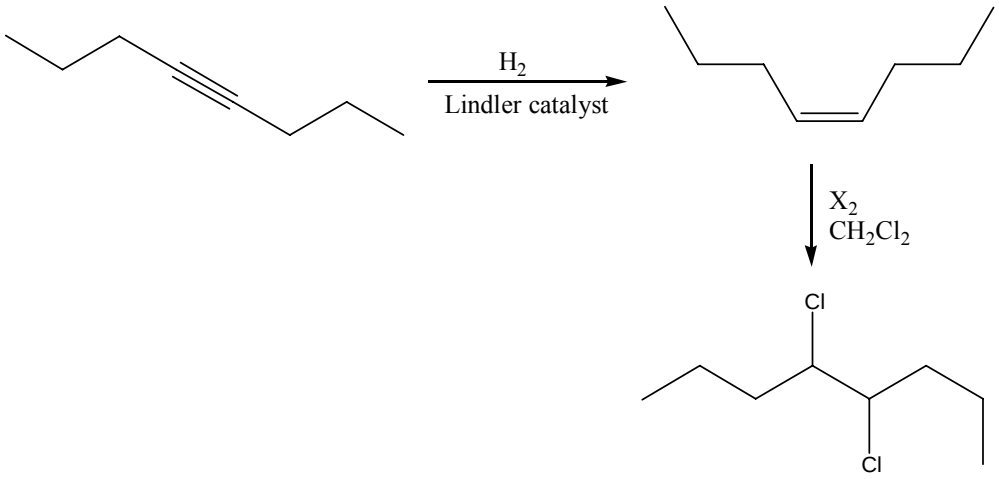
(c)



(d)



(e)

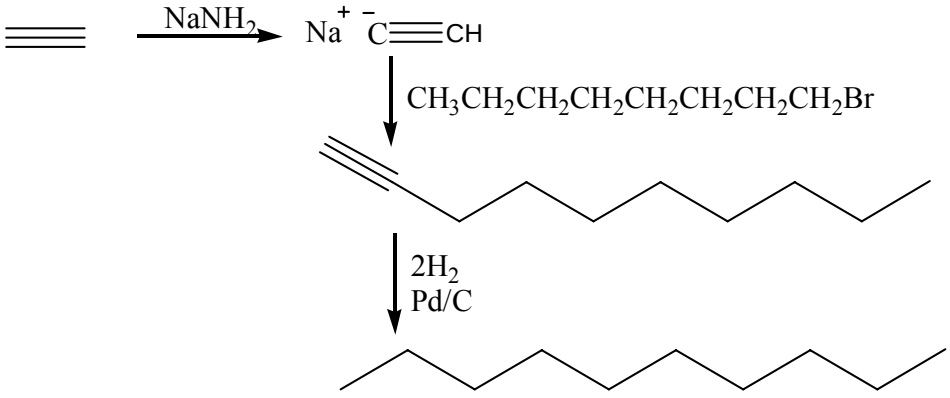


8.14 Beginning with acetylene and any alkyl halides needed, how would you synthesize the following compounds?

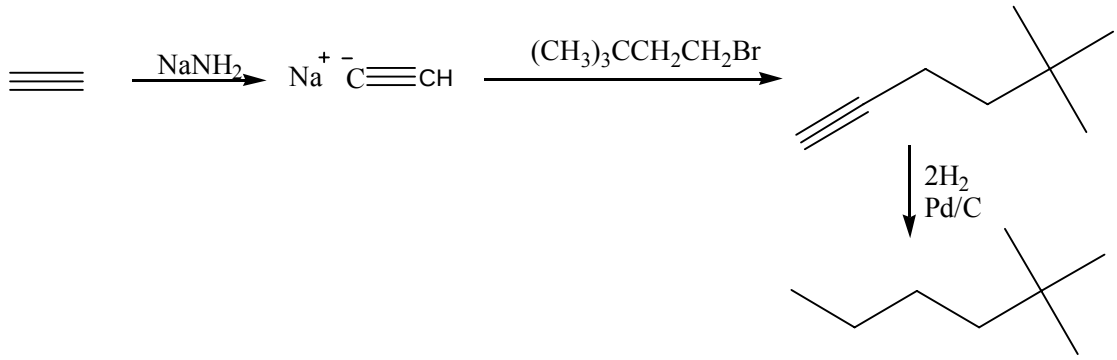
(a) Decane (b) 2,2-Dimethylhexane

(c) Hexanal (d) 2-Heptanone

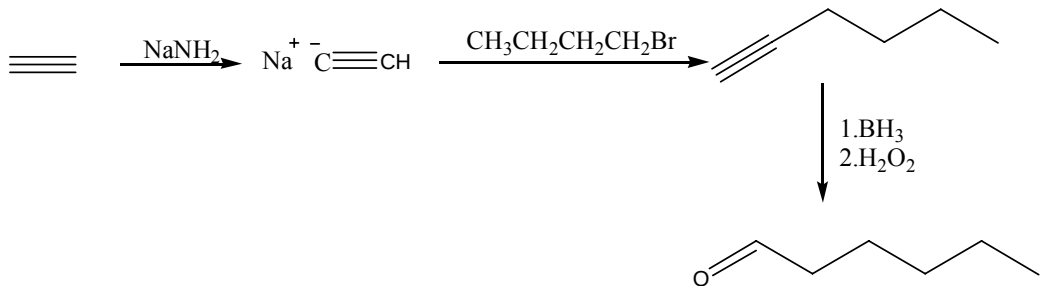
Solution: (a)



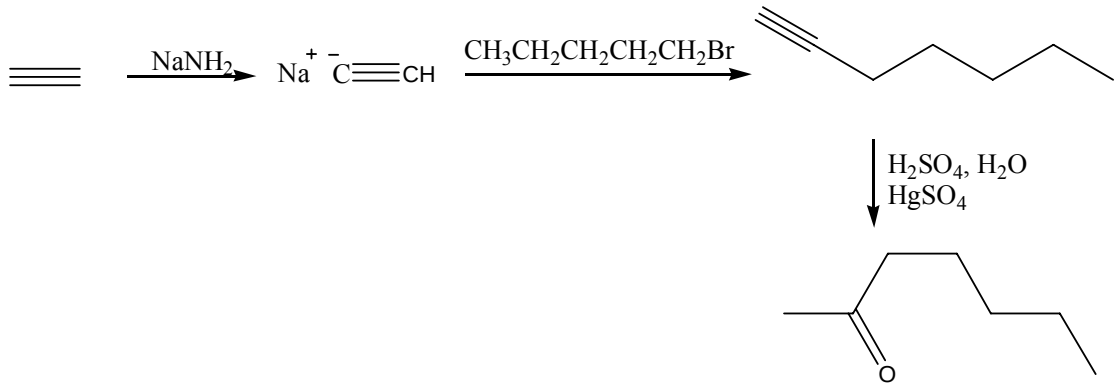
(b)



(c)

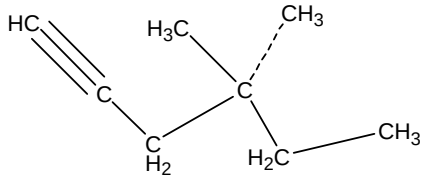


(d)

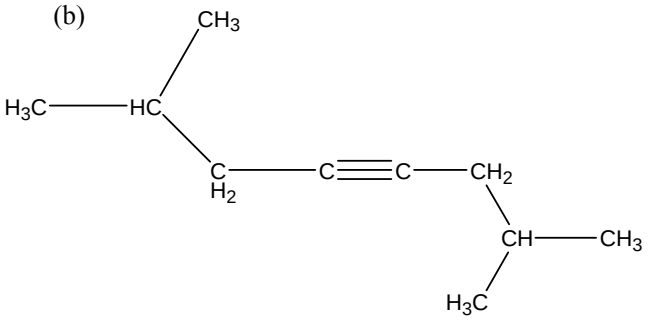


8.15 Name the following alkynes, and predict the products of their reaction with (i) H_2 in the presence of a Lindlar catalyst and (ii) H_3O^+ in the presence of $HgSO_4$:

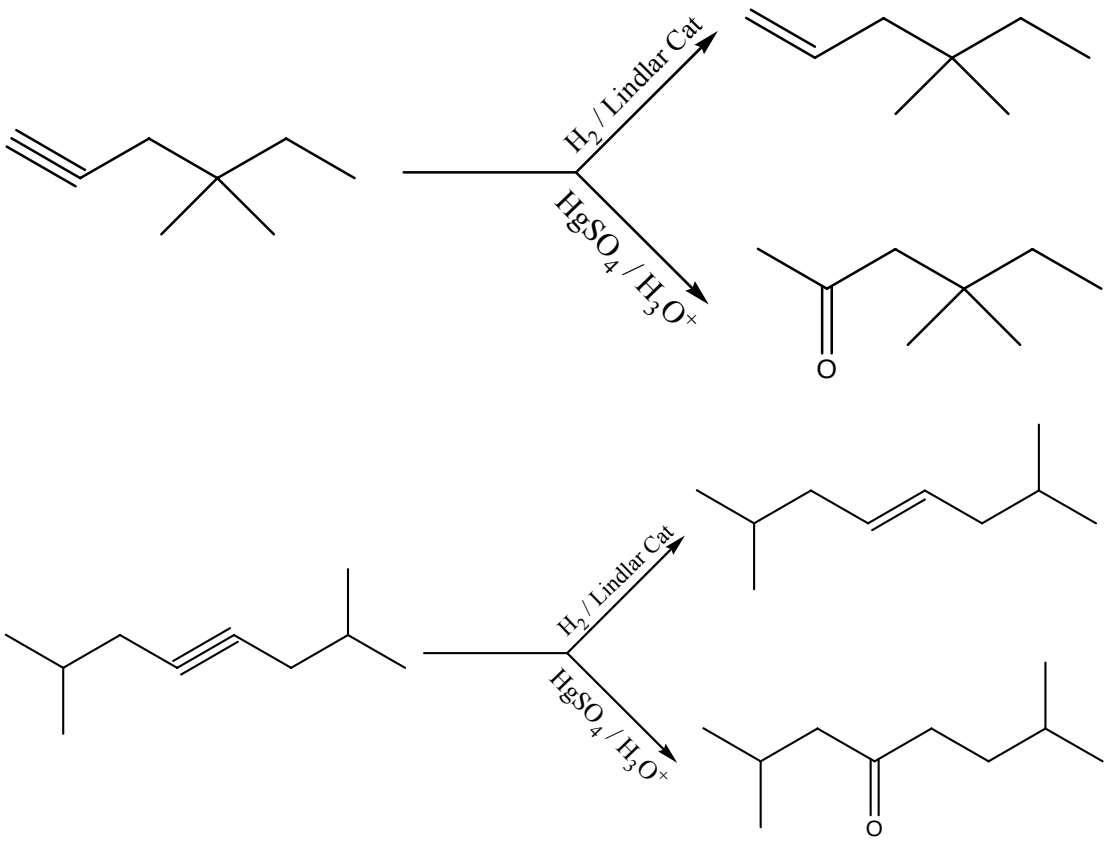
(a)



(b)

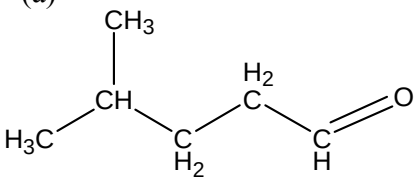


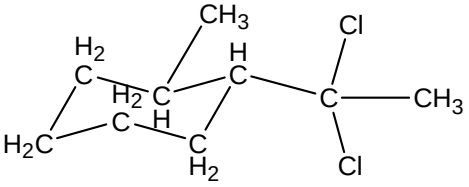
Solution:



8.16 From what alkyne might each of the following substances have been made?

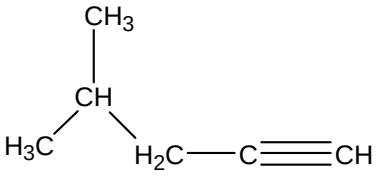
(a) (b)



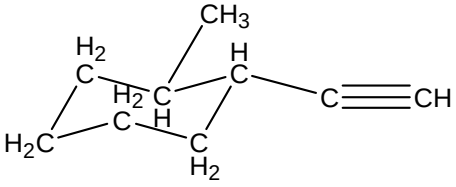


Solution:

(a) is from



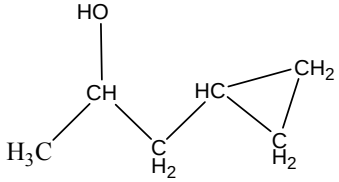
4-Methyl-pentyne and (b) is from



1-Ethynyl-2-methyl-cyclohexane

8.17 How would you prepare the following substances, starting from any compounds having four carbons or fewer?

(a)



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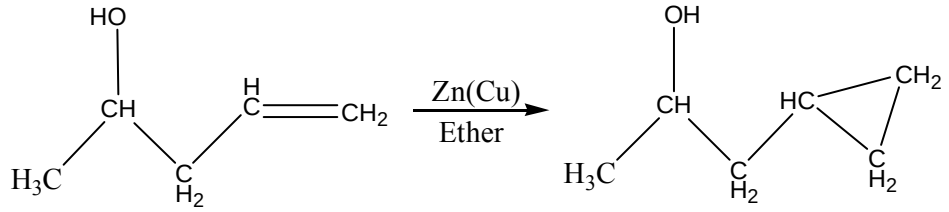
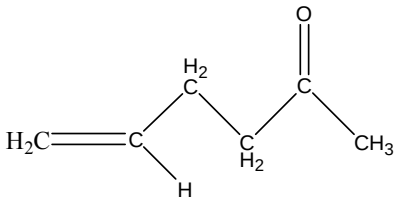
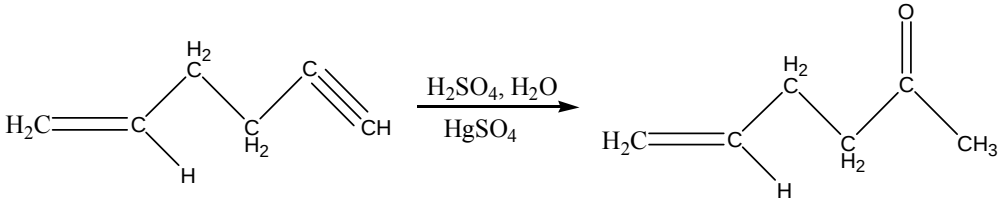


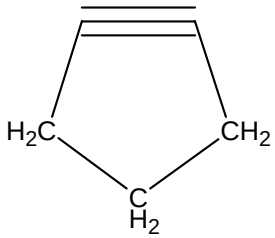
(b)



Solution:



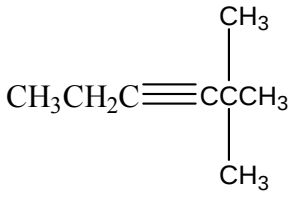
8.18 The following cycloalkyne is too unstable to exist. Explain.

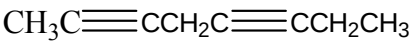


Solution: It's not possible to form a small ring containing a triple bond because the angle strain that would result from bending the bonds of an SP-hybridized carbon to form a small ring is too great.

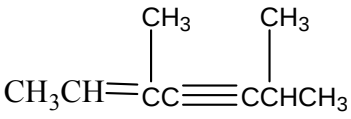
8.19 Give IUPAC names for the following compounds.

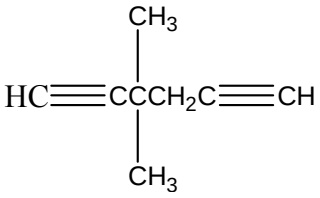
a.

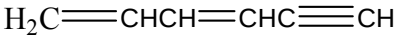


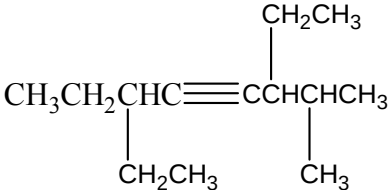
b. 

c.



d. 

e. 

f. 

Solution:

a. 2,2-Dimethyl-3-hexyne

b. 2,5-Octadiyne

c. 3,6-Dimethyl-2-heptene-4-yne

d. 3,3-Dimethyl-1,5-hexadiyne

e. 1,3-Hexadiene-5-yne

f. 3,6-Diethyl-2-methyl-4-octyne

8.20 Draw structures corresponding to the following names:

a. 3,3-Dimethyl-4-octyne

b. 3-Ethyl-5-methyl-1,6,8-decatriyne

c. 2,2,5,5-Tetramethyl-3-hexyne

d. 3,4-Dimethylcyclodecyne

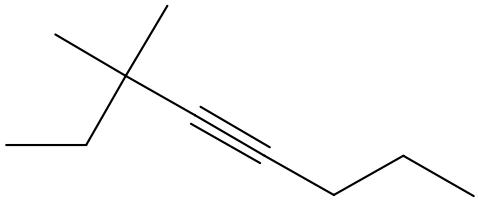
e. 3,5-Heptadien-1-yne

f. 3-Chloro-4,4-dimethyl-1-nonen-6-yne

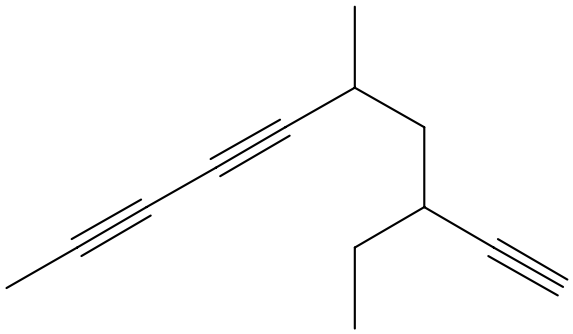
g. 3-sec-Butyl-1-heptyne

h. 5-tert-Butyl-2-methyl-3-octyne

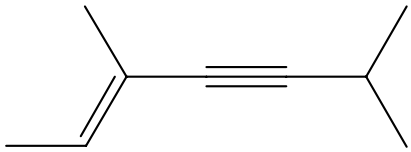
Solution:

a. 

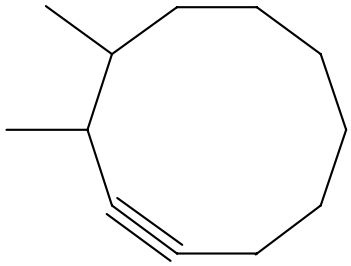
3,3-Dimethyl-4-octyne



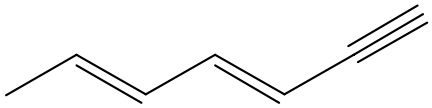
b. 3-Ethyl-5-methyl-1,6,8-decatriyne



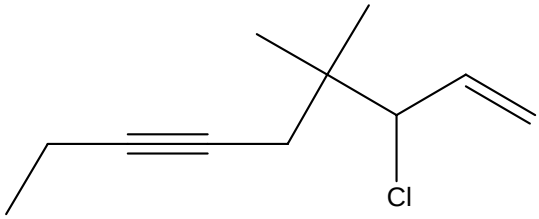
c. 3,6-Dimethyl-2-heptene-4-yne



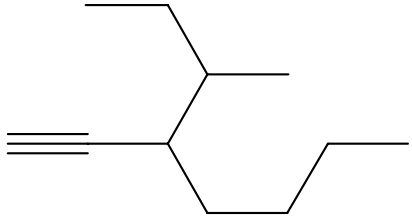
d. 3,4-Dimethylcyclodecyne



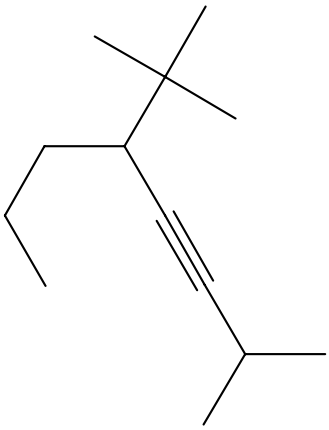
e. 3,5-Heptadien-1-yne



f. 3-Chloro-4,4-dimethyl-1-nonen-6-yne



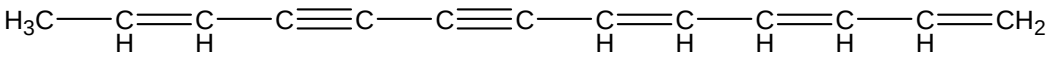
g. 3-sec-Butyl-1-heptyne



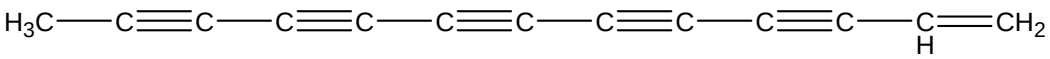
h. 5-tert-Butyl-2-methyl-3-octyne

8.21 The following two hydrocarbons have been isolated from various plants in the sunflower family. Name them according to IUPAC rules.

(a)



(b)

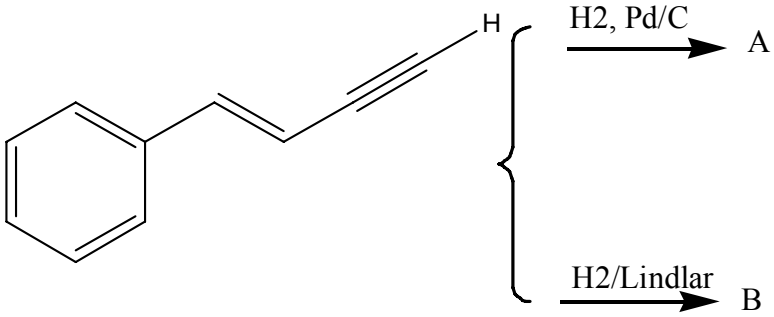


SOLUTION:

(a) (3E, 5E, 11E)-1,3,5,11-Tridecatetraen-7, 9-diyne.

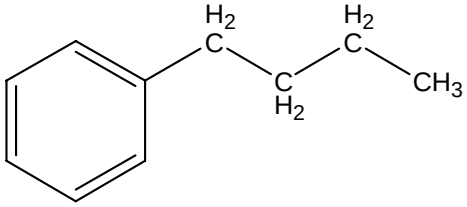
(b) 1-Tridecene-3, 5, 7, 9, 11-pentayne

8.22. Predict the products of the following reactions.

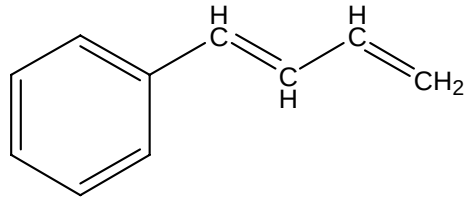


SOLUTION:

A:



B:



8.23 A hydrocarbon of unknown structure has the formula C8H10. On catalytic hydrogenation over the Lindlar catalyst, 1 equivalent of H2 is absorbed. On hydrogenation over a palladium catalyst, 3 equivalents of H2 are absorbed.

a) How many degrees of unsaturation are present in the unknown?

b) How many triple bonds are present?

c) How many double bonds are present?

d) How many rings are present?

e) Draw a structure that fits the data.

Solution:

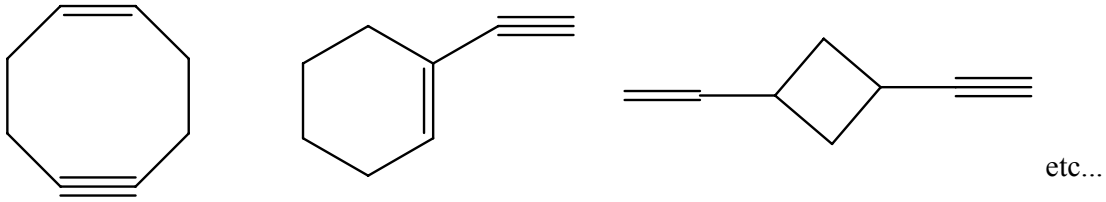
a) 4 degrees of unsaturation are present.

b) 1 triple bond is present.

c) 1 double bond is present.

d) 1 ring is present.

e) The possible structure can be:



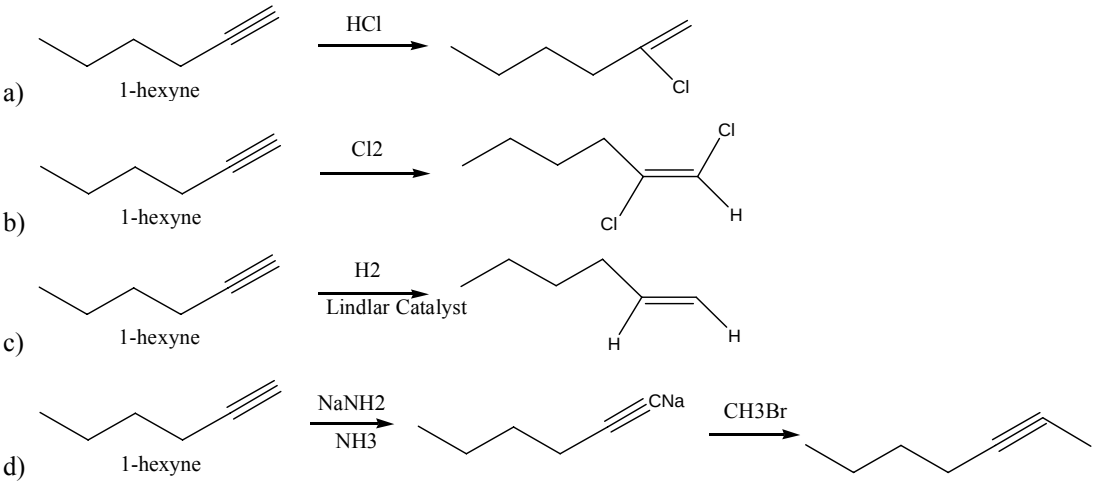
8.24 Predict the products from reaction of 1-hexyne with the following reagents:

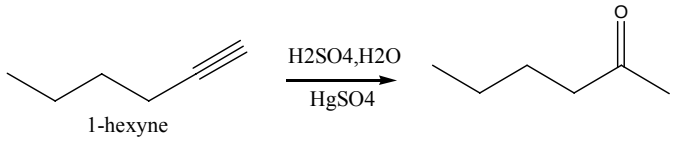
a) 1 equiv HBr b) 1 equiv Cl2

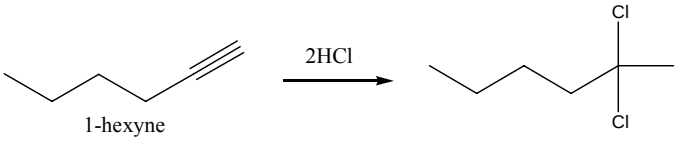
c) H2, Lindlare catalyst d) NaNH2, in NH3, the CH3Br

e) H2O, H2SO4, HgSO4 f)2 equiv HCl

Solution:



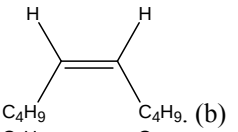
e) 

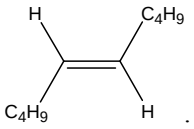
f) 

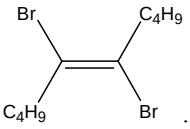
8.25 Predict the products from reaction of 5-decyne with the following reagents:

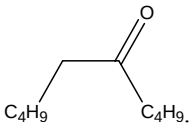
(a) H_2, Lindlar catalyst. (b) Li in NH_3. (c) 1 equiv Br_2. (d) BH_3 in THF, then H_2O_2, OH-. (e) H_2O, H_2SO_4, $HgSO_4$. (f) Excess H_2, Pd/C catalyst.

Solution:

(a) 

. (b) 

. (c) 

. (d) 

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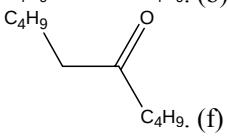
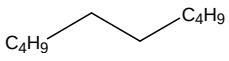
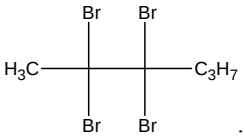
(e) 

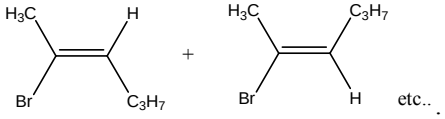
. (f) 

8.26 Predict the products from reaction of 2-hexyne with following reagents:

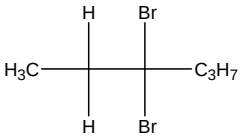
(a) 2 equiv Br_2. (b) 1 equiv HBr. (c) Excess HBr. (d) Li in NH_3. (e) H_2O, H_2SO_4, $HgSO_4$

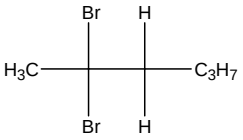
Solution:

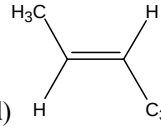
(a) 

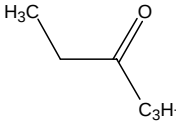
. (b) 

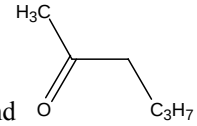
etc..

(c) 

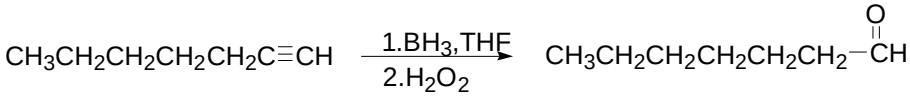
and 

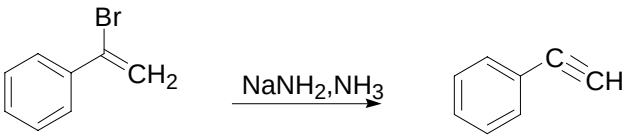
(d) 

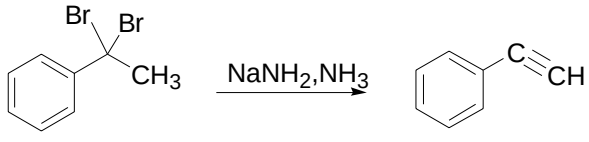
. (e) 

and 

8.27 Predict the products of the following reactions:

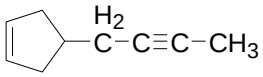
(a) 

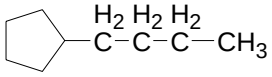
(b) 

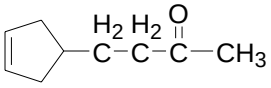
(c) 

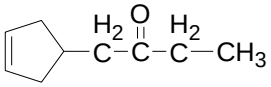
8.28 Hydrocarbon A has the formula C_9H_{12} and absorbs 3 equivalents of to yield B, C_9H_{18} ,when hydrogenated over a Pd/C catalyst. On treatment of A with aqueous H_2SO_4 in the presence of mercury(II), two isomeric ketones, C and D, are produced. Oxidation of A with $KMnO_4$ gives a mixture of acetic acid (CH_3CO_2H) and the tricarboxylic acid E. Propose structure for compounds A-D, and write the reactions.

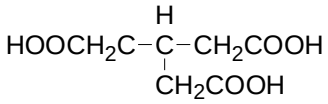
Solution:

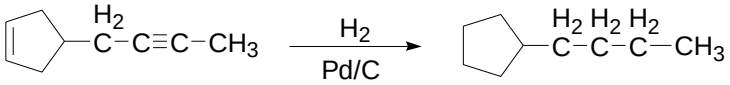
A 

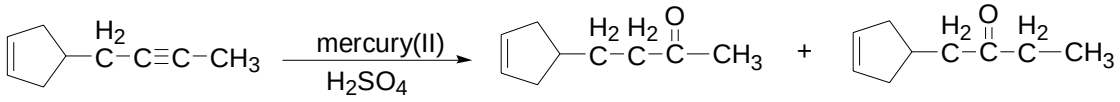
B 

C 

D 

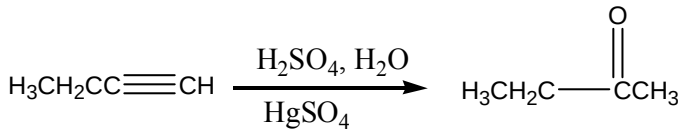
E 

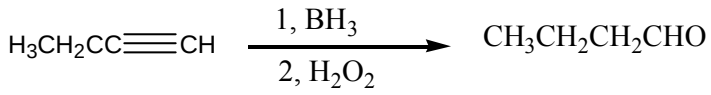
(1) 

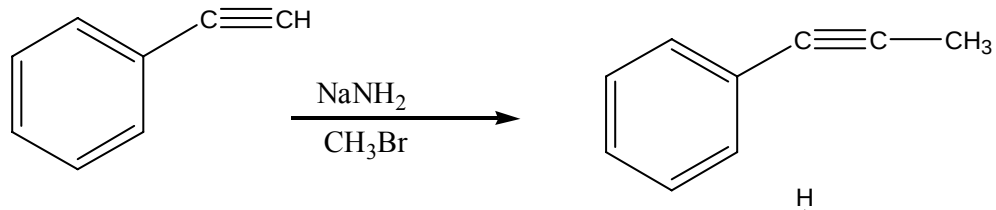
(2) 

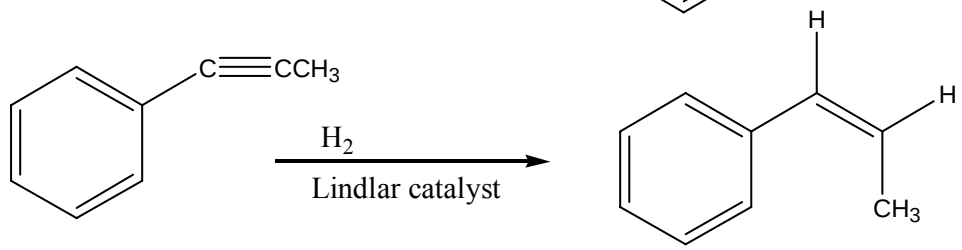
(3) 

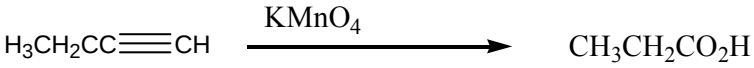
8.29 How would you carry out the following reactions?

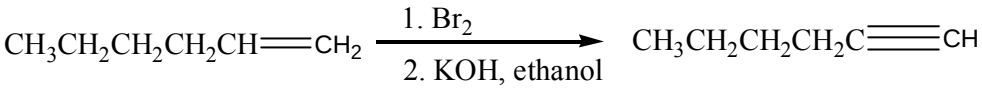
(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

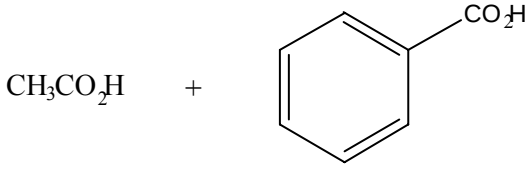
8.30 Occasionally, chemists need to invert the stereochemistry of an alkene, that is, to convert a cis alkene to trans alkene, or vice versa. There is no one-step method for doing an alkene inversion, but the transformation can be carried out by combining several reactions in the proper sequence. How would you carry out the following reactions?

(a) trans-5-Decene $\xrightarrow[\text{2. KOH, ethanol}\\\text{3. } H_2\text{, Lindlar catalyst}]{\text{1. } Br_2}$ cis-5-Decene

(b) cis-5-Decene $\xrightarrow[\text{2. KOH, ethanol}\\\text{3. Li, } NH_3]{\text{1. } Br_2}$ trans-5-Decene

8.31 Propose structures for hydrocarbons that give the following products on oxidative cleavage by $KmnO_4$ or O_3

(a) $CO_2 + CH_3(CH_2)_5CO_2H$



(b)

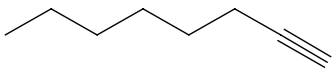
(c) $HO_2(CH_2)_8CO_2H$

(d) $CH_3CHO + CH_3COCH_2CH_2CO_2H + CO_2$

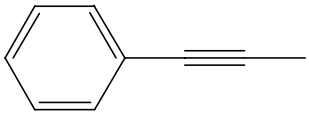
(e) $OHCCH_2CH_2CH_2CH_2COCO_2H + CO_2$

Solution:

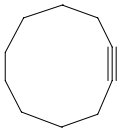
(a)



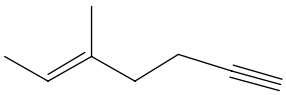
(b)



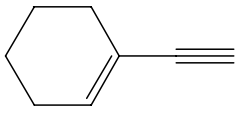
(c)



(d)

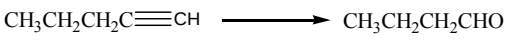


(e)

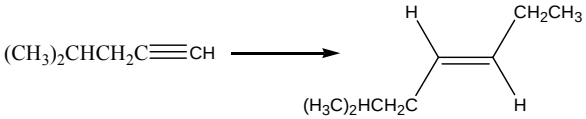


8.32 Each of the following syntheses requires more than one step. How would you carry them out?

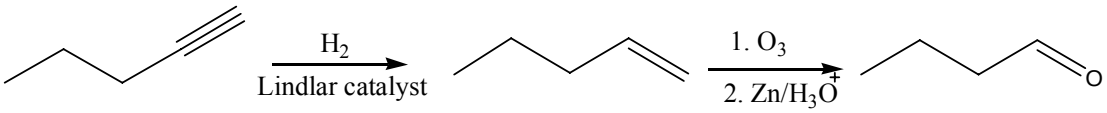
(a)



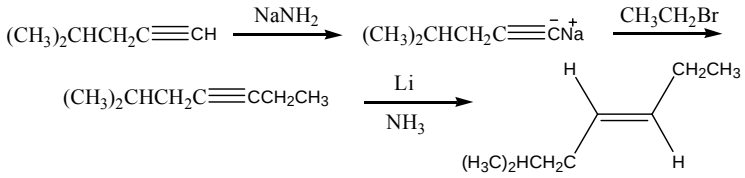
(B)



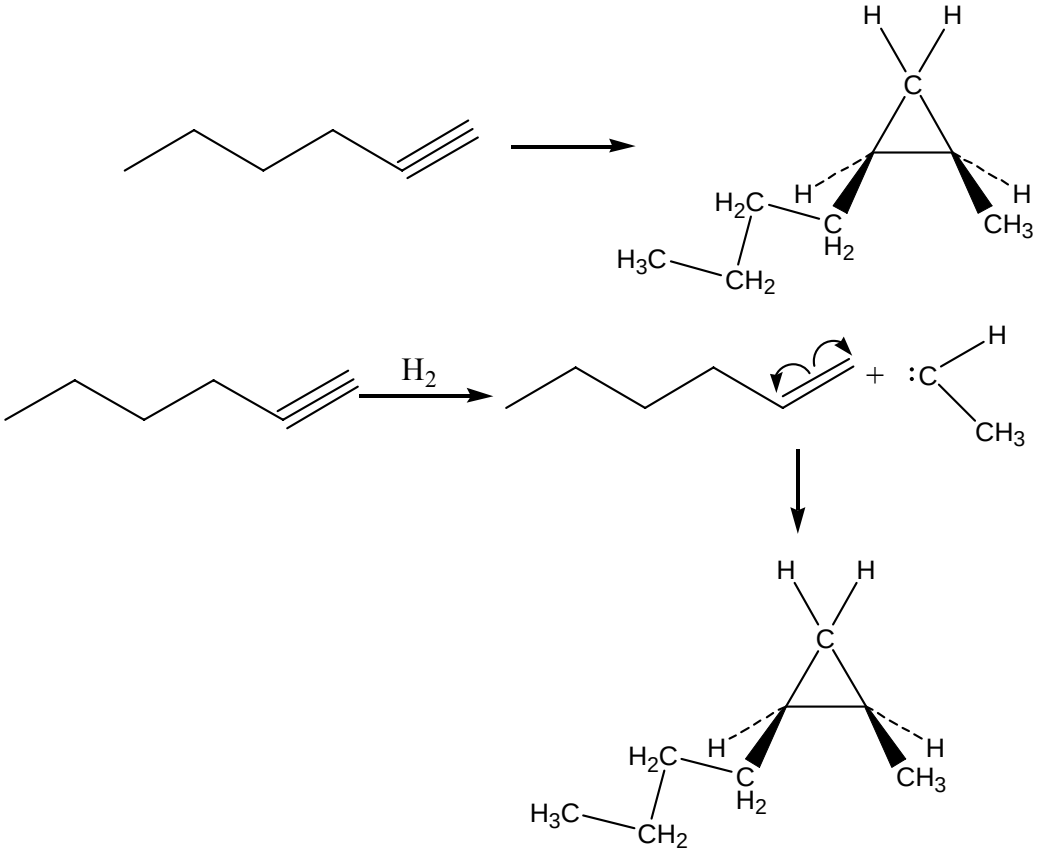
Solution: (a)



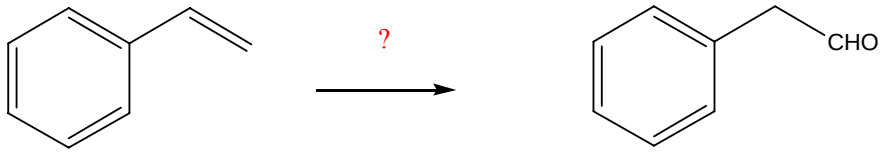
(b)



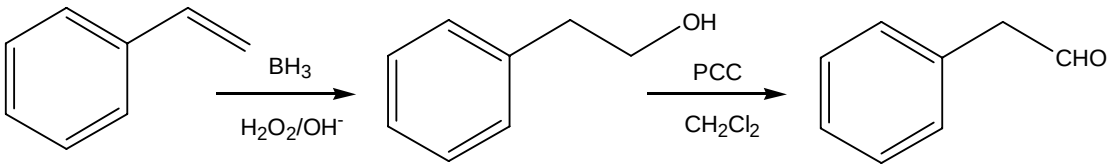
8.33 How would you carry out the following transformation? More than one step is needed.



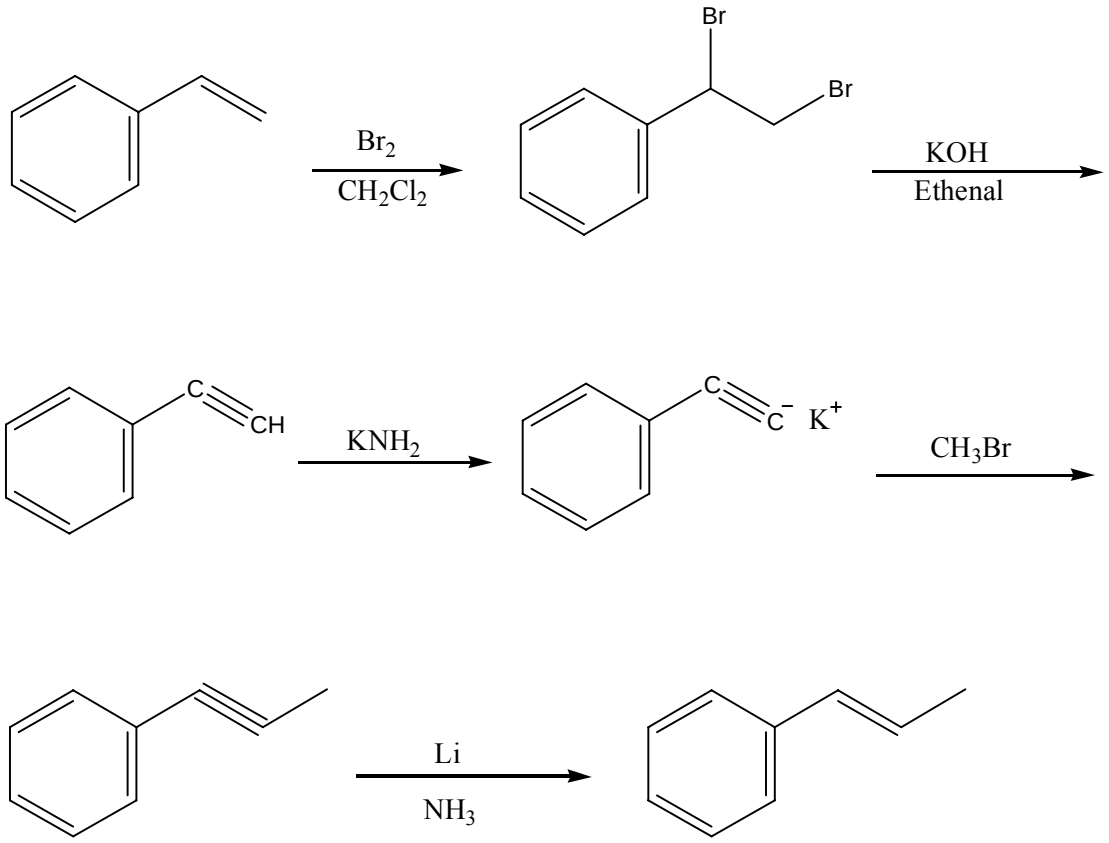
8.34 How could you carry out the follow conversion? More than one step is needed.



Solution:



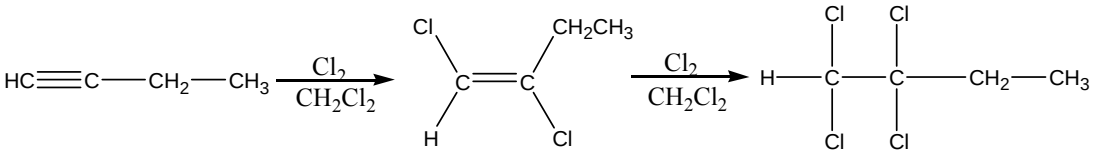
8.35 How would you carry out the following transformation? More than one step is needed.



8.36 Synthesize the following compounds using 1-butyne as the only source of carbon, along with any inorganic reagents you need. More than one step may be needed.

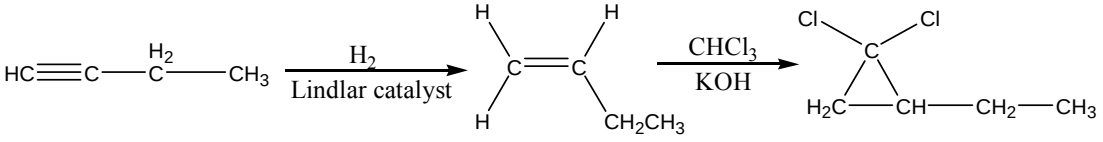
(a) 1, 1, 2, 2-Tetrachlorobutane

Solution:



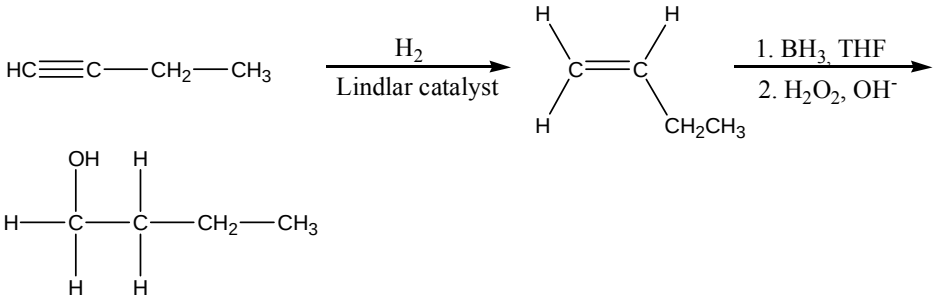
(b) 1, 1-Dichloro-2-ethylcyclopropane

Solution:



(c) Butanal

Solution：



8.37 How would you synthesize the following compounds from Acetylene and any alkyl halides with four or fewer carbons? More than one step may be required.

(a) $CH_3CH_2CH_2C{\equiv}CH$ (b) $CH_3CH_2C{\equiv}CCH_2CH_3$

(c) $(CH_3)_2CHCH_2CH{=}CH_2$ (d) $CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_3$

(e) $CH_3CH_2CH_2CH_2CH_2CHO$

Solution: (a)

$$HC{\equiv}CH \xrightarrow[NH_3]{NaNH_2} HC{\equiv}C^-Na^+ \xrightarrow[THF]{CH_3CH_2CH_2Br} CH_3CH_2CH_2C{\equiv}CH$$

(b)

$$HC{\equiv}CH \xrightarrow[NH_3]{NaNH_2} HC{\equiv}C^-Na^+ \xrightarrow[THF]{CH_3CH_2Br} CH_3CH_2C{\equiv}CH \xrightarrow[NH_3]{NaNH_2} CH_3CH_2C{\equiv}C^-Na^+ \xrightarrow[THF]{CH_3CH_2Br} CH_3CH_2C{\equiv}CCH_2CH_3$$

(c)

$$HC{\equiv}CH \xrightarrow[NH_3]{NaNH_2} HC{\equiv}C^-Na^+ \xrightarrow{(CH_3)_2CHCH_2Br} (CH_3)_2CHCH_2C{\equiv}CH \xrightarrow[\text{Lindlar catalyst}]{H_2} (CH_3)_2CHCH_2CH{=}CH_2$$

(d)

$$HC{\equiv}CH \xrightarrow[NH_3]{NaNH_2} HC{\equiv}C^-Na^+ \xrightarrow[THF]{CH_3CH_2CH_2Br} CH_3CH_2CH_2C{\equiv}CH \xrightarrow[NH_3]{NaNH_2} CH_3CH_2CH_2C{\equiv}C^-Na^+ \xrightarrow[THF]{CH_3CH_2CH_2Br}$$

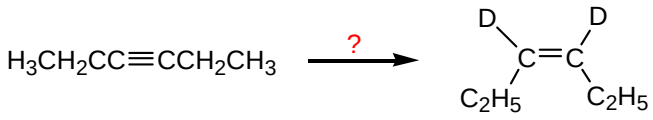
$$CH_3CH_2CH_2C{\equiv}CCH_2CH_2CH_3 \xrightarrow[HgSO_4]{H_2SO_4,H_2O} CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_3$$

(e)

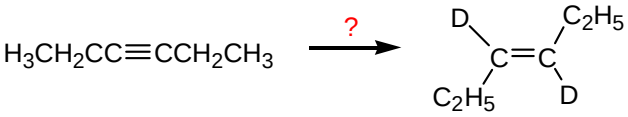
$$HC{\equiv}CH \xrightarrow[NH_3]{NaNH_2} HC{\equiv}C^-Na^+ \xrightarrow[THF]{CH_3CH_2CH_2CH_2Br} CH_3CH_2CH_2CH_2C{\equiv}CH \xrightarrow[2.H_2O_2]{1.BH_3} CH_3CH_2CH_2CH_2CH_2CHO$$

8.38 How would you carry out the following reactions to introduce deuterium into organic molecules?

(a)



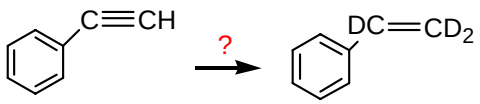
(b)



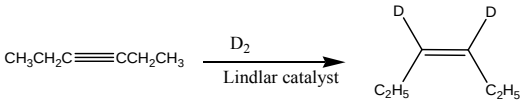
(c)

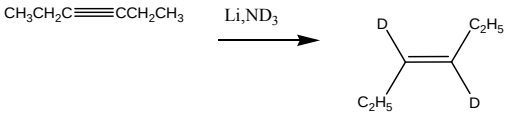
$$H_3CH_2CH_2CC{\equiv}CH \xrightarrow{?} H_3CH_2CH_2CC{\equiv}CD$$

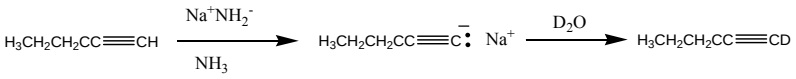
(d)

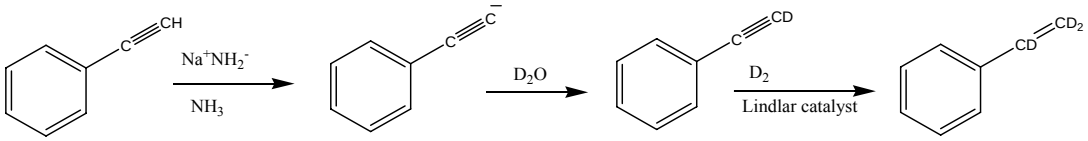


Solution:



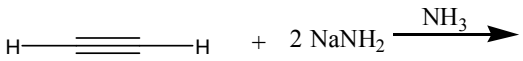


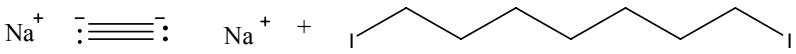


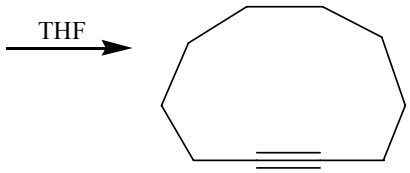


8.39 How would you prepare cyclodecyne starting from acetylene and any alkyl halide needed?

Solution:



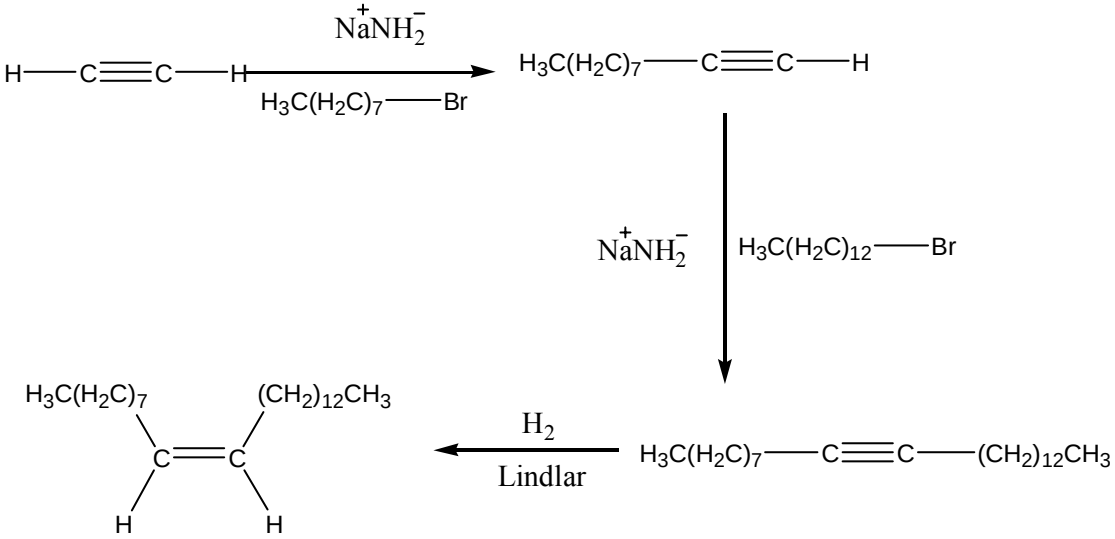




8.40 The sex attractant given off by the common housefly is an alkene named muscalure. Propose a synthesis of muscalure starting from acetylene and any alkyl halides needed. What is the IUPAC name for muscalure?

cis- $H_3C(H_2C)_7HC{=}{=}CH(CH_2)_{12}CH_3$

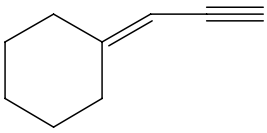
Solution: The IUPAC name for muscalure is cis-9-tricosene.



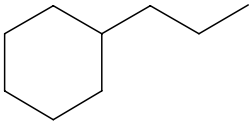
8.41 Compound A (C_9H_{12}) absorbed 3 equivalents of H on catalytic reduction over a palladium catalyst to give B (C_9H_{18}). On ozonolysis , compound A gave, among other things, a ketone that was identified as cyclohexanone. On treatment with, gave C ($C_{10}H_{14}$) .Give the structure of A, B, C.

Solution:

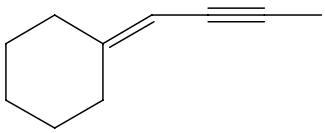
A:



B:

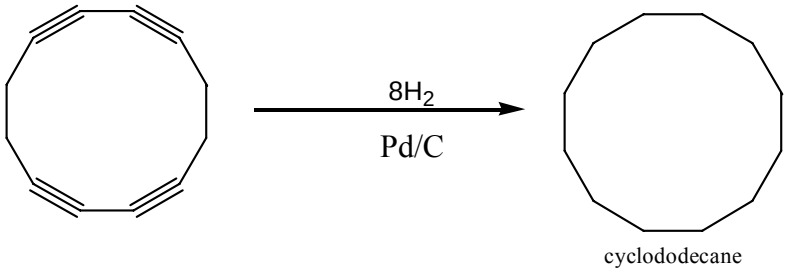


C:

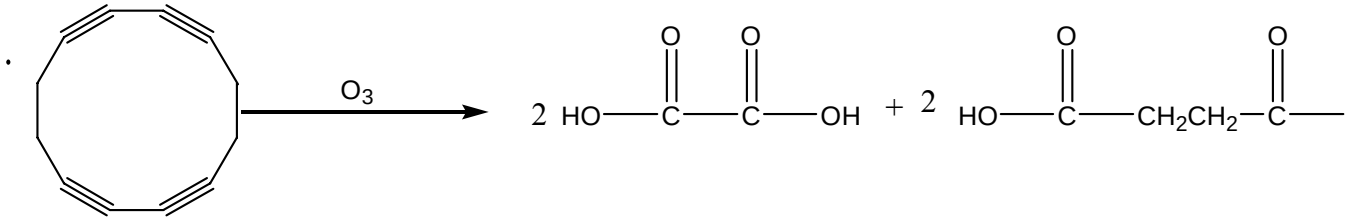


8.42 Hydrocarbon A has the formula C12H8. It absorbs 8 equivalents of H2 on catalytic reduction over a palladium catalyst. On ozonolysis, only two products are formed: oxalic acid (HO2CCO2H) and succinic acid (HO2CCH2CH2CO2H). Write the reactions, and propose a structure for A.

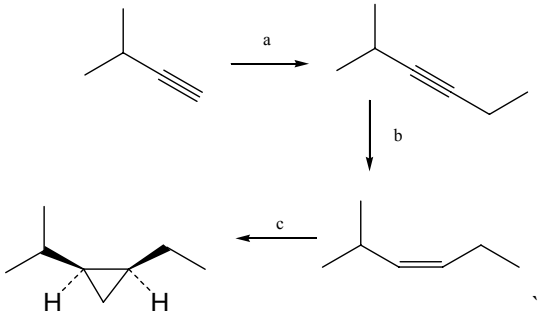
Slution:



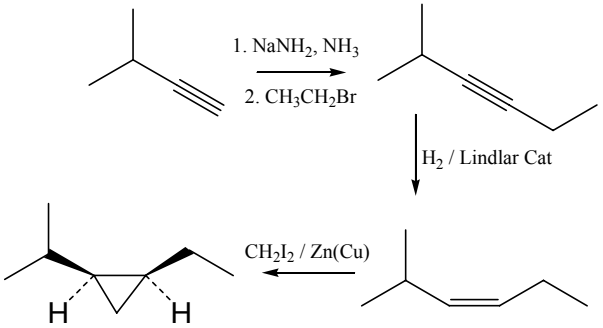
cyclododecane



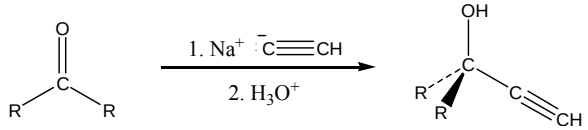
8.43 Identify the reagents a-c in the following scheme:



Solution:

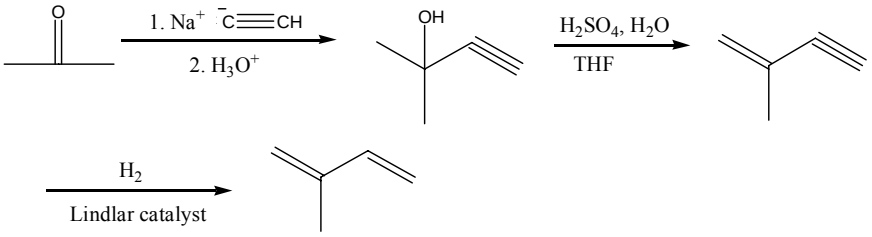


8.44 Organometallic reagents such as sodium acetylide undergo an addition reaction with ketones, give alcohols:



How might you use this reaction to prepare 2-methyl-1,3-butadiene, the starting material used in the manufacture of synthetic rubber

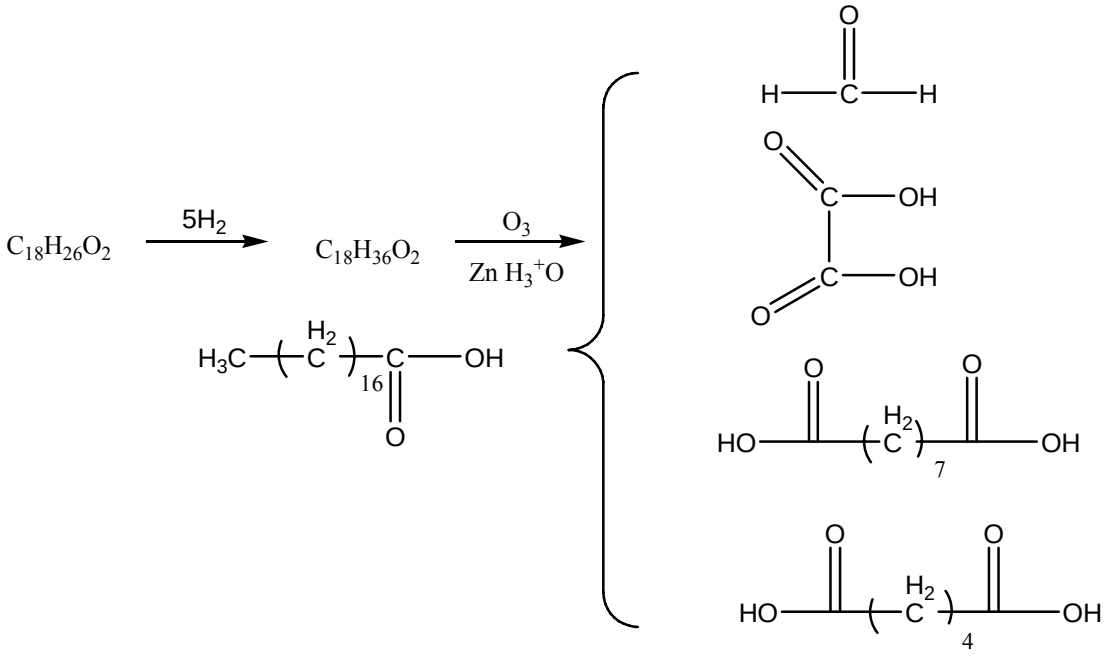
Solution：



8.45 Erythrogenic acid, C18H26O2, is an acetylenic fatty acid that turns a vivid red on exposure to light. On catalytic hydrogenation over a palladium catalyst, 5 equivalents of H2 are absorbed, and stearic acid, CH3(CH2)16CO2H, is produced. Ozonolysis of erythrogenic acid gives four products: formaldehyde, CH2O; oxalic acid, HO2CCO2H; azelaic acid , HO2C (CH2)7CO2H; and the aldehyde acid OHC(CH2)4CO2H. Draw two possible structures for erythrogenic acid, and suggest a way to tell them apart by carrying out some simple reactions.

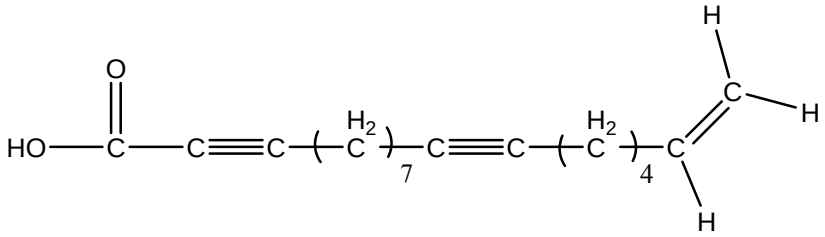
Solution

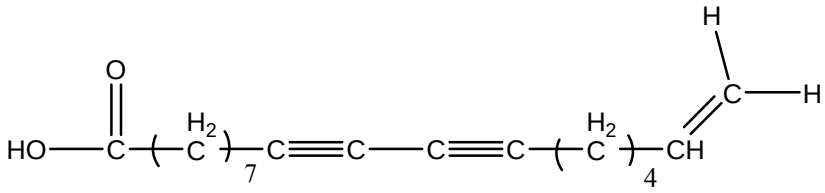
The problem can be described as following illustration:



And first we can predict the unsaturated degree of starting material by the fact that it can absorb 5 H2 and form a carboxylic acid. So The molecular has 5 double bonds or 1 triple bond and 3 double bonds or 2 triple bonds and 1 double bond besides a C=O bond, and there is no rings in the molecular.

Second we can think about the products after it is treated with O_3 ,and we can get the solultion t the problem.





You can see two possible starting materials according to the problem exactly. However, we can tell them apart from each other by following method.

STEP1

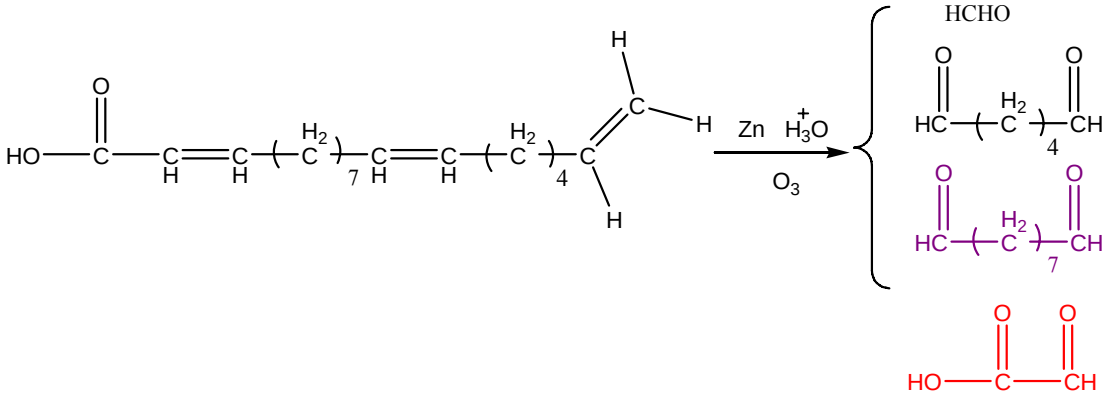
Treat the SM with Lindlar catalyst, and then we can get the product only contains double bond but no triple bond.

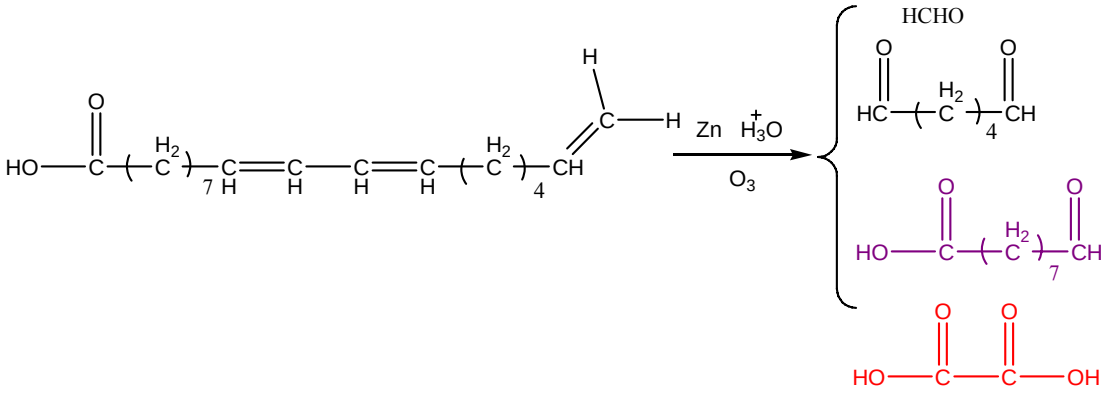
STEP2

Treat the product get from the step with O3 ,H3O+ and Zn and then we can get the products following.

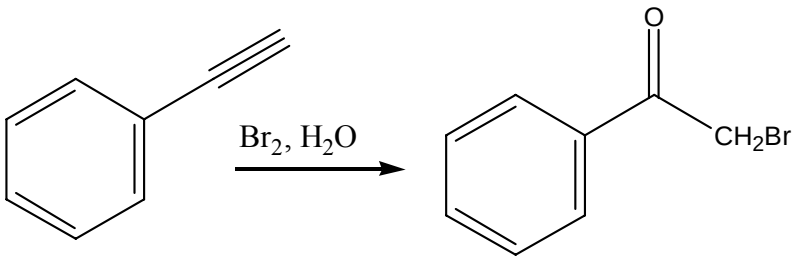
STEP3

Analyze the products and you can find the differences written following between the different SMs . At last we can tell them apart easily.



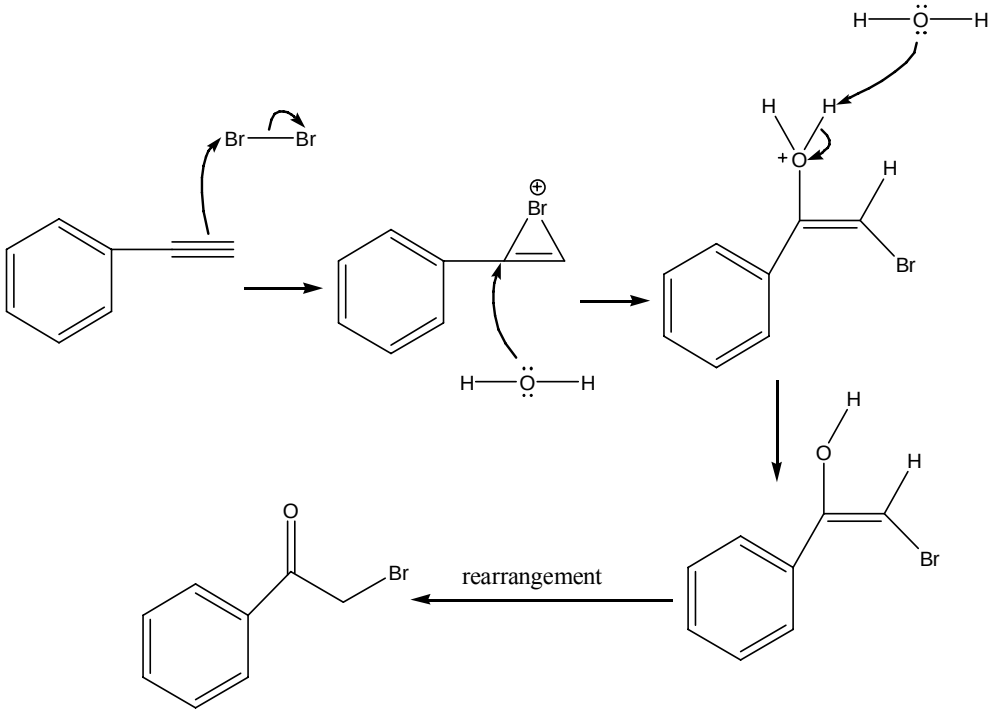


8.46 Terminal alkynes react with Br_2 and water to yield bromo ketones. For example:



Propose a mechanism for the reaction. To what reaction of alkenes is the process analogous?

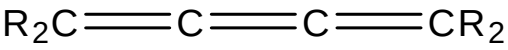
Solution:



The mechanism here is just like the halohydrin of alkene.

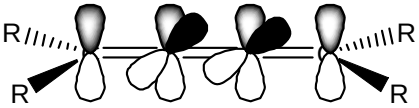
8.47 A cumulene is a compound with three adjacent double bonds. Draw an orbital picture of cumulene. What kind of hydridization do the two central carbon atoms have? What is the geometric relationship of the substituents on one end to the substituents on the other end? What kind of isomerism

is possible?



Solution:

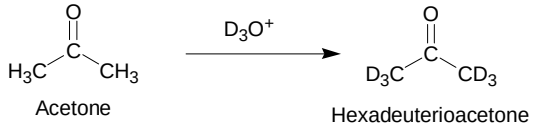
(a) They are sp hybridized.



(b) The geometric relationship of the substituents on one end to the substituents on the other end is cis and trans.

(c) Stereoisomers.

8.48 Reaction of acetone with D3O+ yields hexadeuterioacetone. This is, all the hydrogens in acetone are exchanged for deuterium. Review the mechanism of alkyne hydration, and then propose a mechanism for this deuterium incorporation.



Solution: